PART I - OIL FROM COAL

COAL-TO-OIL LABORATORIES AND PILOT PLANTS, BRUCETON, PA.

The laboratory and pilot-plant work at Bruceton on gas synthesis to produce liquid fuels from coal has included: Pilot-plant production of gasoline by Fischer-Tropsch synthesis with a nitrided fused-iron catalyst; simultaneous removal of carbon dioxide and hydrogen sulfide from raw synthesis gas by hot carbonate solution; laboratory study of catalysts and their preparation, treatment, and activity; and studies on the separation and identification of products of the Fischer-Tropsch synthesis.

In pilot-plant work on direct hydrogenation of coal to gasoline, some of the difficulty from "coke" deposition was obviated by redesign of the reaction system. In studies on the structure and chemistry of coal, microorganisms were found which can utilize extracts from lignites and fractions from coal hydrogenation. Lithium in ethylenediamine was found to be a powerful reducing system for organic compounds, and is experimentally convenient and versatile.

Synthesis of Liquid Fuels From Hydrogen and Carbon Monoxide

(Fischer-Tropsch and Related Processes)

Process Development

Pilot-Plant Operations

Oil-Circulation Test With Nitrided-Iron Catalyst. - In the oil-circulation process the catalyst is immersed in the coolant oil. The circulating oil removes the heat of reaction from the catalyst zone to an external heat exchanger, where the heat is recovered by generation of high-pressure steam. Many engineering problems of the process have been solved, and the pilot plant is now being used to obtain engineering data on improved catalysts as these are developed.

In previous smaller scale Fischer-Tropsch tests nitrided-iron catalysts have been found to be very durable and to produce high yields of oxygenated compounds, principally alcohols. Furthermore, blending such alcohols with gasoline is known to be an effective way to increase the octane rating. If gasoline that contains a high concentration of alcohol can be produced, economy will thus be realized by minimizing or possibly eliminating the need for adding tetraethyl lead, or a premium gasoline may be obtained by the addition of tetraethyl lead.

An extended experiment with a nitrided fused-iron catalyst has been run in the oil-circulation pilot plant. The catalyst was prepared by reducing it in hydrogen at 450° C. and then nitriding it in ammonia at 325° C. A number of operating variables, such as temperature, pressure, space velocity, rate of conversion, rate of gas recycle, synthesis-gas composition, carbon dioxide scrubbing, and reflux removal, were investigated.

The yield of oxygenated compounds was high - 40 percent of the total C_{3+} hydrocarbons plus oxygenates. The composition of the oxygenates was: Alcohols 85 to 92 percent, aldehydes plus ketones 3 to 8 percent, esters 1 to 6 percent, and acids less than 1 percent. With the nitrided catalyst the C_{3+} product contained a higher percentage of gasoline (82.9 percent) than the product obtained in prior runs with the reduced catalyst (55.0 percent). The finished gasoline, which contained the alcohol, had an octane number of 92.9; after addition of 1 ml. of tetraethyl lead per gallon of gasoline the octane number increased to 98.5.

When the pressure was raised from 300 to 400 p.s.i.g., the space-time yield or total productivity was increased; but the rates of oxidation and attrition of the catalyst also increased. The activity and selectivity of the nitrided catalyst remained essentially constant during 3,700 hours of synthesis. This operating period was more than double the life of granular reduced-iron catalysts.

Hot Carbonate Process for Purifying Synthesis Gas. - The removal of carbon dioxide and hydrogen sulfide from gas mixtures is a necessary step in the synthesis of liquid fuels from coal by the Fischer-Tropsch process. About 200 cubic feet of carbon dioxide must be removed for each gallon of liquid fuel produced. Carbon dioxide in synthesis gas acts as a diluent and in high concentrations may be detrimental to the life and activity of the catalyst.

A process in which a hot, concentrated solution of potassium carbonate is used as the purification agent has been investigated during the past several years. In this process absorption takes place at an elevated pressure (300 to 400 p.s.i.g.) and at approximately the same temperature as the regeneration (80° to 120° C.). Therefore, no heating and cooling of the solution are necessary, less steam is required than for the monoethanolamine process, and expensive heat exchangers can be eliminated. The pilot plant for this process was described in the 1953 annual report, and the effect of the operating variables upon steam consumption was shown in the 1954 report.

Simultaneous removal of carbon dioxide and hydrogen sulfide was investigated this year with mixtures prepared to contain concentrations of these impurities that may occur in raw synthesis gas. About the same efficiency of removal (maximum, 97 percent) was obtained for the 2 components. More thorough removal of hydrogen sulfide was achieved when the carbon dioxide in the scrubbed gas had been reduced to low concentrations. Carbon dioxide concentrations of 0.1 to 0.2 percent in the purified gas have been achieved by thoroughly regenerating the spent solution. Under these conditions steam consumption is only about one-half of that required for purification with monoethanolamine.

Bench-Scale Experiments

Catalyst-Oil Slurry Process. - In the slurry process finely ground catalyst particles are suspended in heavy cooling oil. Such a system is flexible, and heat generated during synthesis can be easily removed. However, under certain conditions the catalyst has settled out or caked on the reactor walls as a result of agglomeration of the catalyst particles, and several potential solutions to this problem have been studied. Improved performance has been achieved with slurry prepared by adding oil to catalyst particles that have been reduced in a dry bed. Use of synthesis product rather than mineral oil has also helped to alleviate agglomeration. The advantage of the synthesis oil may derive from the high-boiling oxygenated materials that it contains, because longer periods of operation were obtained also when a high-molecular-weight alcohol was added to the suspension prepared with mineral oil. The size of the catalyst particles is another factor in the problem of settling. A concentration gradient was found to exist in apparently stable suspensions of fused-iron catalyst, even when the particle size was no larger than 400-mesh.

Forced circulation of the slurry by gas lift aided in maintaining suspension. A concentric inner tube characterized one arrangement. Another modification involved circulation of the slurry by a turbine pump; despite the abrasiveness of the catalyst, no excessive wear was apparent when the pump was dismantled and examined.

Catalyst-Testing Studies

The chemical key of the Fischer-Tropsch synthesis is an active, durable, selective catalyst. During the period covered by this report a number of small-scale experiments were conducted toward development of such catalysts, particularly massive iron catalysts prepared from steel turnings and from steel wool.

Steel Turnings

Various types of alloy-steel turnings were prepared as catalysts by oxidation with steam, impregnation with alkali, and reduction in hydrogen (see fig. 1). In 1954, 1018 carbon-steel turnings impregnated with 0.7 percent copper oxide were reported to be more active than the original turnings without added copper. However, increasing the amount of copper to one percent was found to lower the activity of the catalyst.

Pretreatment. - Carburization of oxidized and alkalized 1018 carbon-steel turnings with pure carbon monoxide at 180° to 350° C. produced a catalyst that was twice as active as reduced turnings and produced large amounts of high-molecular-weight hydrocarbons. A carbonitride prepared from pure carbon monoxide and ammonia was only slightly more active than the reduced turnings; however, its selectivity was characteristic of nitrides.

Treatment of oxidized turnings with a 1-percent nitric acid solution increased the activity of the subsequently alkalized and reduced catalyst from 68 to 114 (arbitrary units) per gram of iron. Treatment with 2.5-percent nitric acid solution was ineffective, with no increase in activity as compared with the untreated turnings.

Fused, Promoted Magnetite

Catalysts produced by fusing of magnetite with various structural promoters were generally no more active than the original fused ore, Alan Wood magnetite, in the reduced and nitrided phases. In these fusions about 3 parts of promoter were added to 100 parts of iron by weight. The starting material, Alan Wood magnetite, contained 0.36 part of SiO_2 and 0.48 part of Al_2O_3 per 100 parts of iron.

Impregnation of reduced and nitrided alumina-promoted iron catalysts with a solution of potassium borohydride did not produce any significant increase in activity or change in selectivity compared with the customary alkali addition.

Particle Size. - With decreasing particle size, activity for both reduced and nitrided catalysts increased to a maximum constant value for particles of 28- to 32-mesh or smaller. The overall selectivity of reduced and nitrided phases did not appear to be affected by particle size.

Temperature of Reduction. - The surface area of reduced catalysts decreased when the reduction temperature was raised from 400° to 625° C. For reduced catalysts the activity appeared to be independent of reduction temperature; for nitrided catalysts the activity decreased sharply at reduction temperatures above 550° C. The reduced catalysts showed no significant change in selectivity; the nitrided catalysts showed a progressive decrease in production of gaseous hydrocarbons with increase in reduction temperature.

Extent of Reduction. - For reduced catalysts the activity increased with extent of reduction up to 40-percent reduction and then became constant. Nitrided catalysts showed a continuous increase in activity with extent of reduction up to at least 60-percent reduction. Selectivity data for the reduced catalysts showed some variation but no definite trend. The C_1 to C_4 hydrocarbons increased with extent of reduction of nitrided catalysts.

Steel-Wool Catalyst

In tests at 269° C. nitrided steel wool was less active than the reduced phase. The product distribution was characteristic of nitrides, with a high yield of gaseous hydrocarbons and large amounts of alcohols in the liquid product. For massive iron catalysts (turnings and steel wool), the activity of nitrides was always less than for the corresponding reduced material.

Sulfur Poisoning of Fischer-Tropsch Catalysts

Although the adverse effect of sulfur compounds on catalysts for the synthesis of hydrocarbons and ammonia has been known for many years, few systematic studies have been made on sulfur poisoning in the Fischer-Tropsch synthesis, especially with iron catalysts. The practical upper limit of concentration of sulfur compounds in synthesis gas apparently has not been determined, and the assumed limiting value of 0.9 grain per 1,000 cubic feet of gas may be lower than is actually required. The iron-water gas catalyst, for example, is known to operate effectively in the presence of relatively high concentrations of sulfur compounds; the high tolerance may be due to the presence of large concentrations of water vapor in this process.

Two types of sulfur poisoning are to be tried in our experiments. In the first the catalyst will be prepoisoned with known concentrations of a sulfur compound dissolved in n-heptane. This method will distribute the sulfur fairly evenly over the catalyst and should provide information regarding the relative poisoning effect of different sulfur compounds. In the second type of experiment a known mixture of synthesis gas and sulfur compound will be passed over the catalyst, and changes during the synthesis will be followed. This method, although similar to poisoning in fixed-bed processes, has the disadvantage that the initial portion of the catalyst acts as a purifying unit and somewhat obscures the interpretation. The twofold approach should provide a fairly complete account of the poisoning phenomenon on iron Fischer-Tropsch catalysts.

Preliminary work has shown that synthesis gas stored in carbon-steel gas cylinders will not retain constant concentrations of sulfur compounds. However, such mixtures can be stored in stainless-steel cylinders for long periods without appreciable changes in sulfur content.

Tests of reduced-iron catalysts immersed in solutions of hydrogen sulfide have indicated that the sulfur was quantitatively adsorbed on the catalyst. Stainless-steel reactors have been fabricated and installed to avoid the removal of sulfur compounds, and stainless-steel gas cylinders have been ordered. The first test of prepoisoned catalysts indicated that catalytic activity was severely reduced by addition of 15 milligrams of sulfur per gram of iron.

Separation and Identification of Fischer-Tropsch Products

Gas Chromatography

Earlier studies on reaction mechanism, at the Bureau and elsewhere, had shown that information regarding the growth of the carbon chain can be obtained from detailed analyses of the C_4 fraction; however, few data have been available on the isomer distribution of Fischer-Tropsch products. Gas chromatography now provides a rapid method for analyzing complex gaseous mixtures in simple, inexpensive apparatus. This method is being used to separate hydrocarbon mixtures from the Fischer-Tropsch synthesis, principally for detailed separation of the C_4 fraction.

The constituents are separated by elution. The sample, with hydrogen as a carrier gas, is passed through a long column of sorbent. The column consists of a 15-foot length of 5/16-inch copper tubing packed with a mixture of sintered kieselguhr and a high-molecular-weight oil (fig. 2). Each component of the sample passes through the column at a rate dependent on its properties of sorption on the packing. Ideally, each should therefore emerge from the column at a different time. In practice, however, two or more components may emerge simultaneously. The apparatus is calibrated with known samples to determine the retention time corresponding to various components. C_1 to C_5 hydrocarbons are collected and measured in a thermal conductivity cell. Certain components are analyzed by mass spectrometer. The method can be modified for analyzing mixtures of organic molecules containing up to about 10 carbon atoms. By combination of gas chromatography with spectrometric methods, detailed analyses of small samples should be possible with small effort.

Analysis of Alcohols

Direct mass spectrometric analysis of alcohols produced in the Fischer-Tropsch synthesis is not possible because of the similarity of mass spectra of hydrocarbons and alcohols. However, trimethylsilyl ethers derived from the alcohols produce distinct mass spectra free of interference by hydrocarbon-type ion fragmentation. Hexamethyldisilazane (I) is useful for converting alcohols to their trimethylsilyl ethers (II):

$$\underset{\text{(I)}}{(CH_3)_3SiNHSi(CH_3)_3} + 2\ ROH \rightarrow 2\ \underset{\text{(II)}}{ROSi(CH_3)_3} + \overline{NH_3}.$$

Mass spectrometric determination of alcohols as their trimethylsilyl ethers present several advantages: Mixtures of alcohols with hydrocarbons can be analyzed directly; the range of the room-temperature mass spectrometer is extended to include C_{10} alcohols; and mixtures of alcohols and water can be analyzed directly, since the water is converted to hexamethyldisiloxane, which has a distinct mass spectrum.

Analysis by the trimethylsilyl ether procedure of alcohols in the oil and aqueous phases from the Fischer-Tropsch synthesis have compared favorable with functional group analysis by infrared spectroscopy. With the room-temperature mass spectrometer the upper limit by this method is C_{10} alcohols. With the new high-temperature mass spectrometer (see fig. 3) this limit will be extended considerably.

Mass Spectra of Acetal-Type Compounds

In the investigation of mixtures of oxygenated compounds the mass spectrum frequently shows peaks that are not attributable to the common alcohols, acids, aldehydes, etc. These peaks always have odd mass numbers and are attributable to

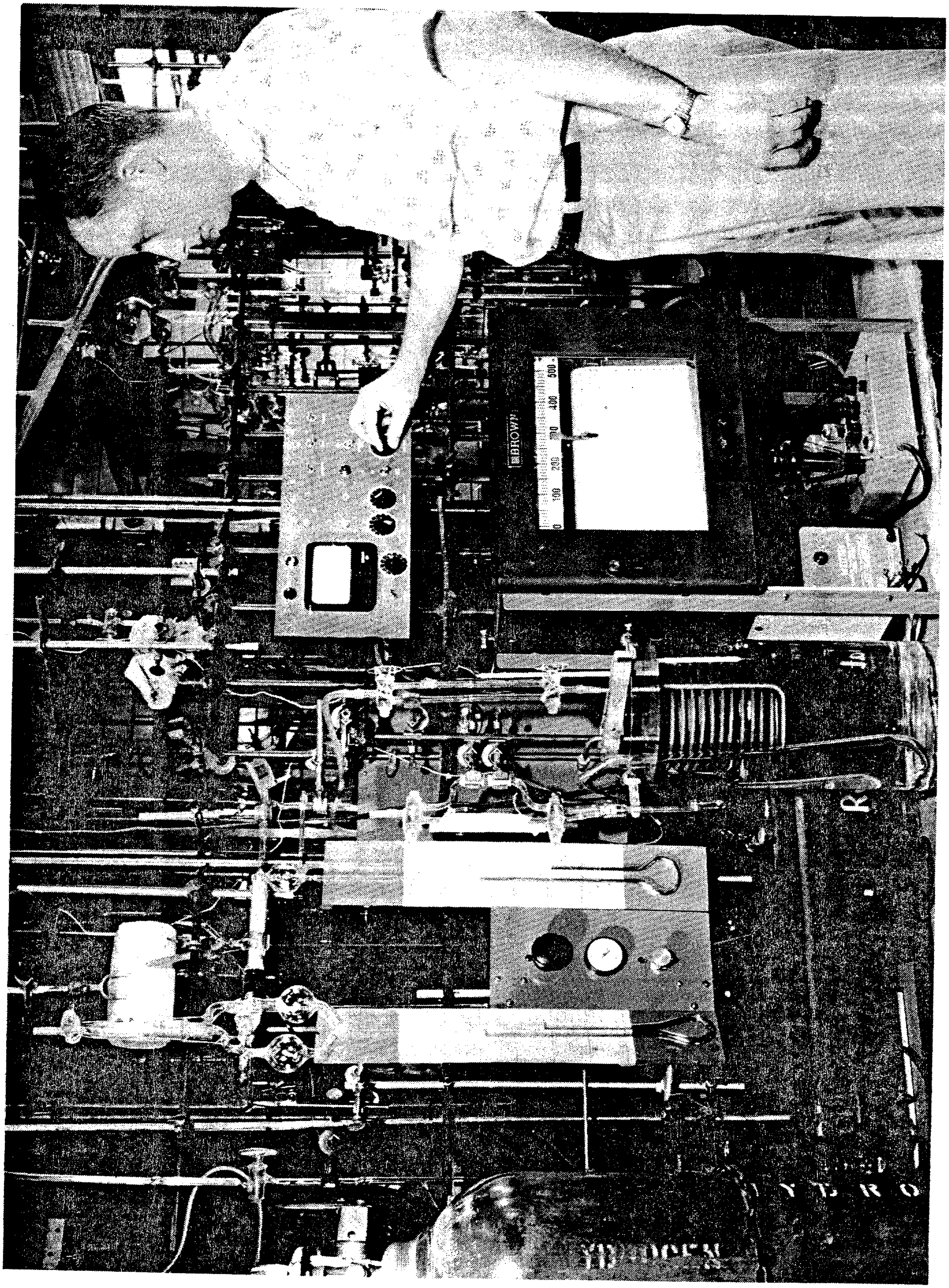


Figure 2. - Gas-chromatography apparatus.

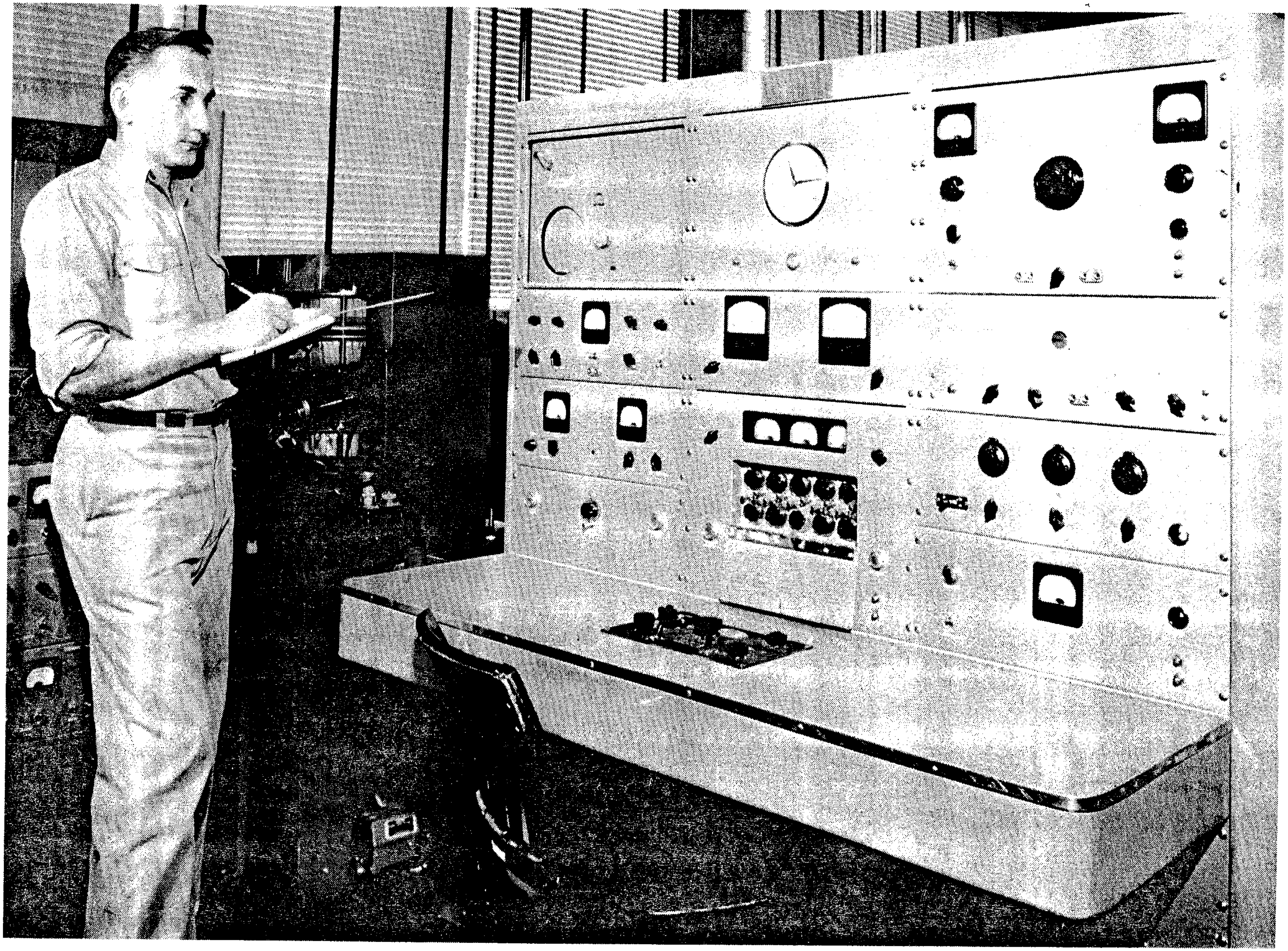


Figure 3. - High-temperature mass spectrometer, used in analyzing organic materials.

fragmentation of molecules. Furthermore, these unknown peaks are consistently two mass units higher than peaks from alcohols and acids. The unknown oxygenated hydrocarbons that produce such peaks must contain two oxygen atoms and no unsaturated bonds; acetals and hemiacetals are logical possibilities. Mixing aldehydes and alcohols produces hemiacetals, most of which are neither stable nor isolable. Anomalous mass peaks in spectra of these mixtures are attributable to hemiacetals. An empirical correlation based on fragmentation has been developed and utilized for the identification of acetals.

Evidence has been found for the existence of moderately stable hemiacetals in the vapor state. The decomposition of gaseous hemiacetals has been followed by mass spectrometer; the rate is first order, and rate constants have been calculated for dimethyl formal and for dimethyl acetal. Alcohol-aldehyde mixtures can be analyzed, despite hemiacetal formation, after the vapor phase hemiacetal has decomposed.

Chemistry of Metal Carbonyls

In further study of the chemistry of the oxo process, infrared spectroscopy has been used to elucidate the structures of cobalt carbonyls and hydrocarbonyls. Studies are being made also on the complex molecules that are formed by the reaction of acetylene with cobalt or iron carbonyls, because similar products are believed to occur as intermediates in the Fischer-Tropsch synthesis; information about these compounds may help to explain the mechanism of this synthesis.

Spectra and Structures of Cobalt Carbonyls

Much information on the molecular structures of catalytic materials can be obtained from studies of the catalytic substance and from studies of compounds similar to the catalyst. The spectra and structures of cobalt hydrocarbonyl, dicobalt octacarbonyl, cobalt carbonyl anion, and tetracobalt dodecacarbonyl have been studied. The hydrogen of cobalt hydrocarbonyl is very weakly bound to the rest of the molecule, as shown by infrared spectra and nuclear magnetic resonance studies. The infrared spectrum of cobalt carbonyl anion indicates that the structure is tetrahedral. The wavelength shift of the carbonyl frequency is due to the effect of the ionic charge on the character of the carbonyl bonds. Based on the spectra of dicobalt octacarbonyl, the structure proposed is a trans configuration of two trigonal bipyramids joined at the edge in such a way that the apical and equatorial carbonyls are shared as bridge carbonyls (see fig. 4). The infrared spectrum of tetracobalt dodecacarbonyl is somewhat simpler than that of dicobalt octacarbonyl; the spectrum indicates a structure that contains bridge carbonyls in the ratio of one bridge to two terminal carbonyls.

Iron Carbonyls and Their Derivatives

Previous work with cobalt carbonyls and their derivatives has provided information concerning the mechanism of addition of carbon atoms to unsaturated hydrocarbons and some indications as to the nature of adsorbed intermediates in the Fischer-Tropsch process. Investigations of iron carbonyls and their derivatives are now in progress. The observed difference in chemical reactivity between cobalt and iron hydrocarbonyls may partly explain the different selectivities of cobalt and iron in the Fischer-Tropsch process.

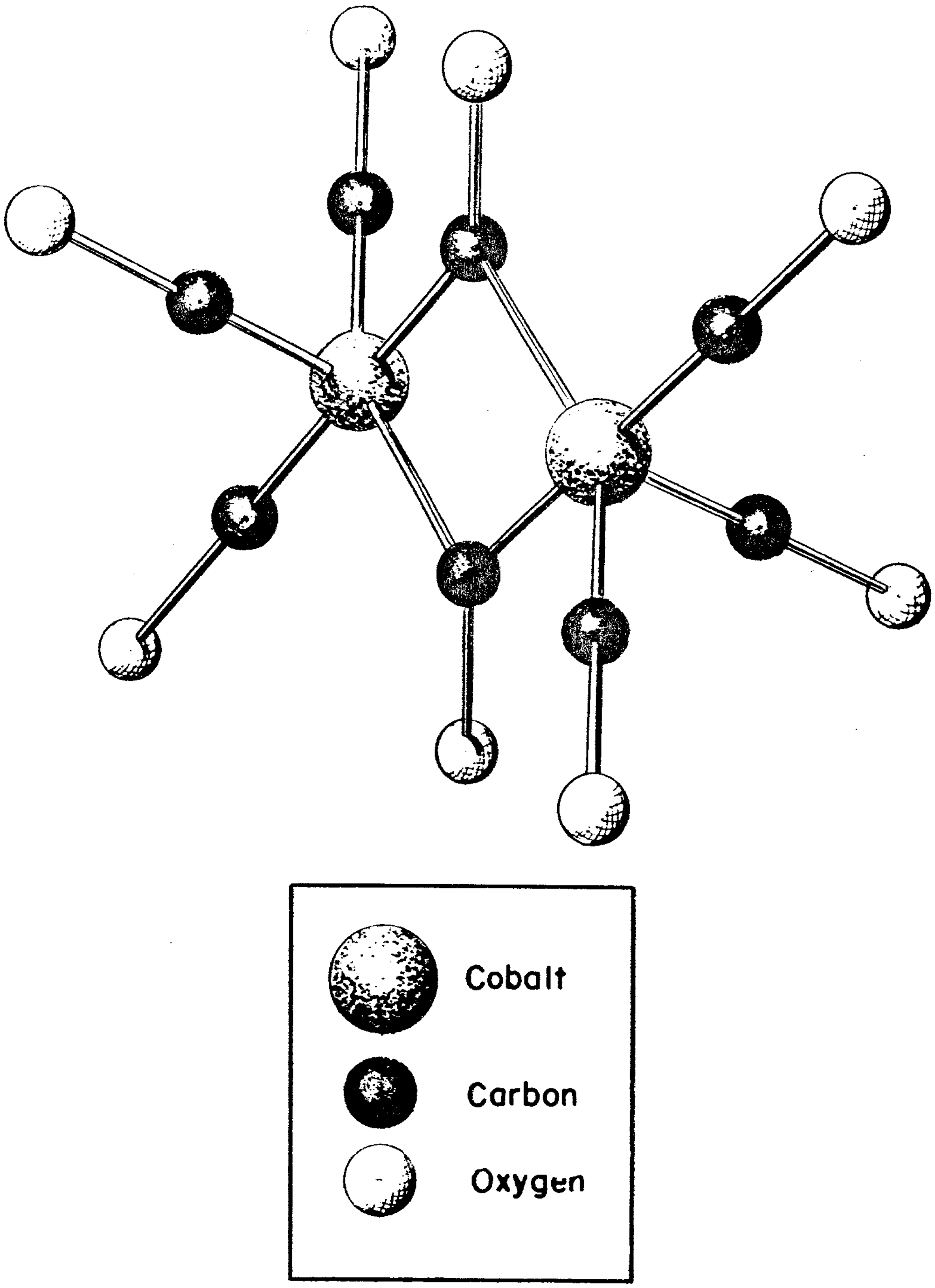
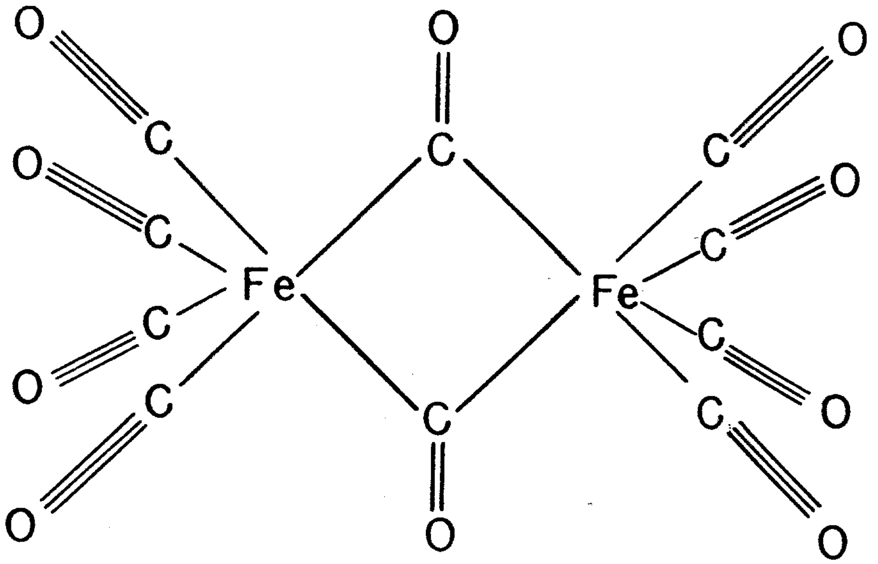


Figure 4. - Structure of dicobalt octacarbonyl.

Iron pentacarbonyl has been found to dissociate in the presence of certain amines according to equation

$$2\mathrm{Fe(CO)_5} \rightleftharpoons \left[\mathrm{Fe(CO)_6}\right]^{++} + \left[\mathrm{Fe(CO)_4}\right]^{=} \qquad (1)$$

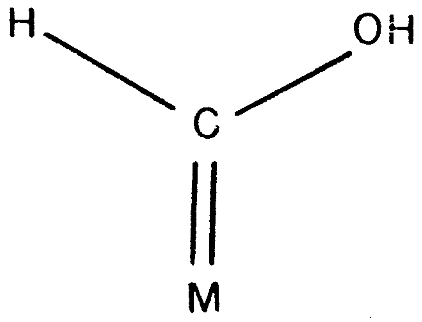
The reaction probably takes place via the formation of an intermediate bridged complex, such as



I

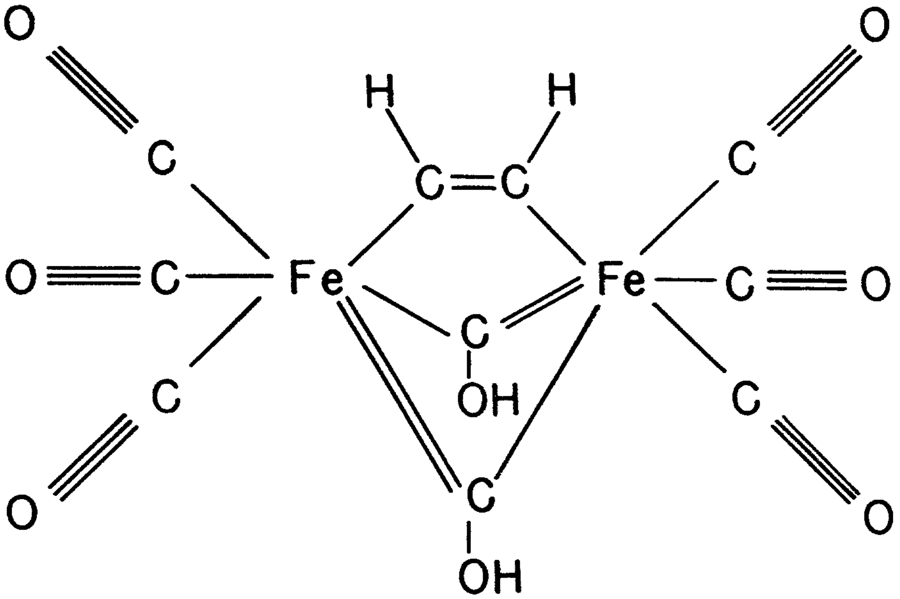
Recent spectroscopic work outside of the Bureau supports the view that bridge carbonyls exist on the catalyst surface. Electron mobility on the catalyst surface is known to play an important part in surface catalysis. The way in which bridge carbonyls may serve as paths for electron transfer is demonstrated by the ionization of iron pentacarbonyls shown above.

An intermediate such as



II.

containing an M=C-OH linkage has been postulated as a surface intermediate in the Fischer-Tropsch reaction. A complex containing this linkage has now been prepared from iron hydrocarbonyl and acetylene and has been shown to possess the structure



III

Complex (III) contains, in one molecule, the catalytic metal, the alkyl metal, the alkyl substrate, and hydrogen and carbon monoxide necessary for chain lengthening. The fact that both of the hydrogen atoms in (III) are acidic and can be replaced by alkali may be useful in studying the role of alkali in the Fischer-Tropsch process.